

The Decomposition of Ozone by Heat.

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Much doubt has recently existed as to the interpretation which may be put upon measurements of the velocity of chemical change in gas reactions. Van't Hoff deduced the "order of the reaction" in certain cases from considerations of the law of mass action. Bone and Wheeler* have shown that the combination of hydrogen and oxygen at temperatures below that necessary to explode the mixture takes place mostly (if not entirely) at the surfaces with which the gases are in contact, and that no conclusion as to the order of the reaction can be drawn from pressure measurements.

Ozone was chosen for further work on the subject, as it affords one of the simplest possible cases. The decomposition by heat furnishes only one substance, and the reaction is irreversible (at least for all practical purposes).

Production of the Ozone.—The ozone was made by means of the usual Siemens' induction tube. Oxygen was obtained by heating potassium chlorate, and was stored over caustic potash solution. The ozonised oxygen was collected over sulphuric acid in a small gas-holder, consisting of two glass bulbs, each of about 350 c.c. capacity, and connected below by a U-tube. One of the bulbs was connected above with a three-way stop-cock, while the other bulb was open to the air through a calcium chloride tube.

The ozone was admitted from the induction tube to the gas-holder through one limb of the three-way stop-cock by means of a ground-glass joint. It was transferred by another ground-glass joint to the decomposition globe through the other limb of the stop-cock.

Apparatus for heating the Ozone.—The ozone was heated in a globe A, of about 350 c.c. capacity, by means of a bath of calcium chloride solution. The globe A was connected with the gauge C, and a similar globe B was connected with the gauge on the other side. The ozone was admitted through the ground-glass joint made at D, and the stop-cock E.

The large globe F and the pressure gauge G were used only for experiments under less than atmospheric pressure. H, K, L, and M represent two-way

* 'Phil. Trans.,' A, vol. 206, p. 1.

diagonal stop-cocks, and N was a small ordinary stop-cock through which sulphuric acid was admitted to the gauge. The bath was heated by an Ostwald burner; it was thoroughly stirred, and the temperature maintained constant to $0^{\circ}.1$.

Method of conducting an Experiment.—The apparatus being in position (as in diagram) and the temperature steady, the globe A was exhausted by means of a Fleuss pump, the globe B being left open to the air. Ozonised oxygen was then transferred from the gas-holder to the globe A. Great care was taken to prevent any moist air from entering. The pressure was regulated so that A was filled at a pressure slightly greater than atmospheric. The excess was allowed to escape through D, the globe A was connected with the gauge, and readings of the pressure were taken at suitable intervals. In order to find the total amount of ozone present, the two globes and gauge were removed from the bath, and the globe A heated for 10 minutes with a Bunsen burner to about 300° (at the lowest part of the globe). In a trial experiment it was found that the ozone remaining after this treatment could be neglected. The apparatus was then replaced in the bath, and after the temperature had become steady, the pressure was read again.

Method of Calculation.—The pressure of the ozone at each reading was calculated as follows:—The actual pressure, as shown by the gauge, at each reading was subtracted from the final reading (when all the ozone was decomposed); double the number obtained gave the pressure of the ozone in millimetres of sulphuric acid.

A correction was then applied for the change of volume of the gases in A and B caused by the movement of the acid in the gauge. The correction was a small one, as the gauge tube was only 2 mm. in diameter.

The first or second order “constants” were then calculated in the usual way. Great difficulty was experienced in obtaining concordant results, especially with a new globe, which usually gave a greater rate of decomposition than it did after some use.

The following results (p. 356, etc.) were obtained at various temperatures; where t = time in minutes, x = amount of ozone decomposed (mm. of H_2SO_4), a = initial pressure of ozone, K_1 is the first order constant $\frac{1}{t} \log \frac{a}{a-x}$, and K_2 the constant of the second order $\frac{x}{t(a-x)a}$:—

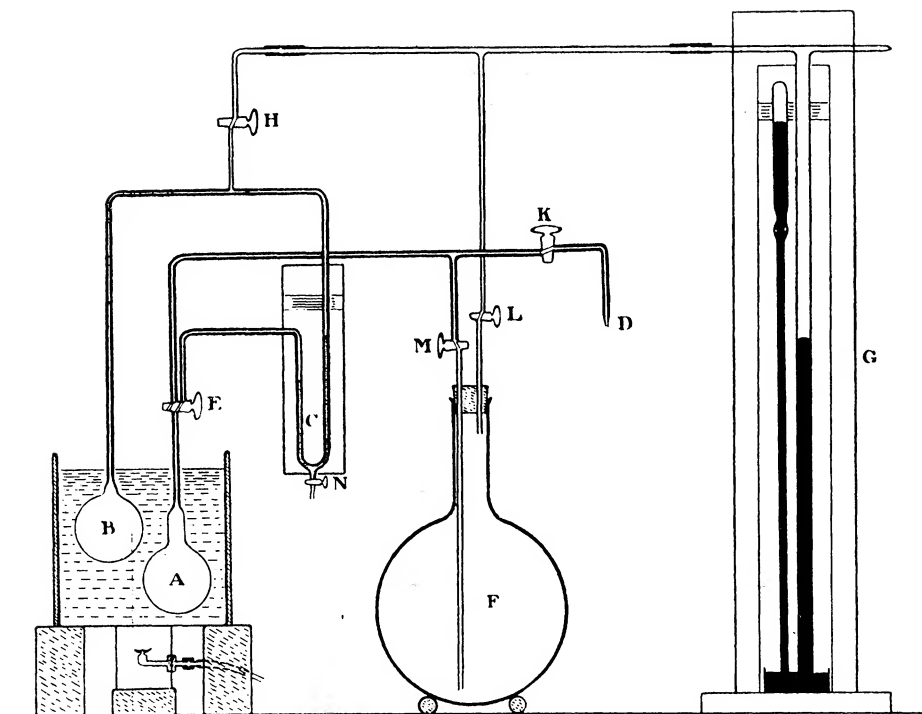


FIG. 1.

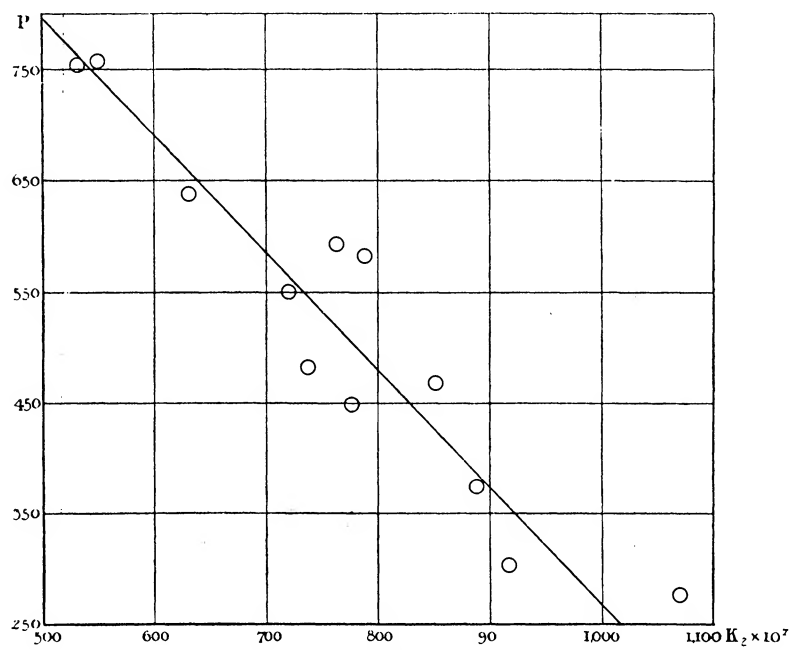


FIG. 2.

Temperature 119°·9. Globe II.

| t . | $a-x$. | x . | $K_2 \times 10^6$. | $K_1 \times 10^4$. |
|-------|---------|----------|---------------------|---------------------|
| 0 | 190·2 | | | |
| 2 | 152·7 | 37·5 | 646 | 477 |
| 3 | 137·4 | 52·8 | 673 | 471 |
| 4 | 124·3 | 65·9 | 697 | 462 |
| 6 | 105·4 | 84·8 | 705 | 427 |
| 8 | 89·2 | 101·0 | 744 | 411 |
| 13 | 64·5 | 125·7 | 788 | 361 |
| 18 | 49·5 | 140·7 | 830 | 325 |
| 28 | 33·3 | 156·9 | 885 | 270 |
| | | Mean ... | 746 | |

Temperature 120°. Globe II.

| t . | $a-x$. | x . | $K_2 \times 10^6$. | $K_1 \times 10^4$. |
|-------|---------|----------|---------------------|---------------------|
| 0 | 227·2 | | | |
| 1 | 199·5 | 27·7 | 611 | 564 |
| 2 | 178·7 | 48·5 | 597 | 521 |
| 3 | 159·0 | 68·2 | 629 | 517 |
| 5 | 130·5 | 96·7 | 652 | 482 |
| 7 | 108·0 | 119·2 | 694 | 461 |
| 12 | 74·0 | 153·2 | 760 | 406 |
| 17 | 54·8 | 172·4 | 815 | 363 |
| 27 | 34·3 | 192·9 | 917 | 304 |
| | | Mean ... | 709 | |

Temperature 100°. Globe II.

| t . | $a-x$. | x . | $K_2 \times 10^7$. | $K_1 \times 10^4$. |
|-------|---------|----------|---------------------|---------------------|
| 0 | 405·1 | | | |
| 2 | 388·8 | 16·3 | 518 | 90 |
| 4 | 372·5 | 32·6 | 540 | 91 |
| 6 | 358·2 | 46·9 | 539 | 89 |
| 11 | 326·2 | 78·9 | 543 | 85 |
| 16 | 299·3 | 105·8 | 545 | 82 |
| 26 | 255·4 | 149·7 | 557 | 77 |
| 41 | 210·2 | 194·9 | 558 | 69 |
| 61 | 168·1 | 237·0 | 570 | 63 |
| 96 | 121·9 | 283·2 | 597 | 54 |
| | | Mean ... | 552 | |

Temperature 80°. Globe II.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^3.$ | $K_1 \times 10^5.$ |
|-----------|-------------|-----------|--------------------|--------------------|
| 0 | 322.9 | | | |
| 15 | 311.4 | 11.5 | 762 | 105 |
| 30 | 301.1 | 21.8 | 748 | 101 |
| 45 | 289.9 | 33.0 | 783 | 104 |
| 60 | 280.2 | 42.7 | 786 | 103 |
| 90 | 262.9 | 60.0 | 785 | 99 |
| 120 | 247.0 | 75.9 | 793 | 97 |
| 180 | 220.3 | 102.6 | 801 | 92 |
| 240 | 198.7 | 124.2 | 806 | 88 |
| 300 | 180.0 | 142.9 | 819 | 85 |
| 360 | 164.5 | 158.4 | 829 | 81 |
| 420 | 151.1 | 171.8 | 838 | 79 |
| 508 | 135.4 | 187.5 | 844 | 74 |
| 568 | 125.2 | 197.7 | 857 | 72 |
| Mean... | | | 804 | |

Temperature 60°.15. Globe II.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^3.$ | $K_1 \times 10^5.$ |
|-----------|-------------|-----------|--------------------|--------------------|
| 0 | 382.5 | | | |
| 180 | 361.2 | 21.3 | 856 | 139 |
| 330 | 344.2 | 38.3 | 881 | 139 |
| 1320 | 264.9 | 117.6 | 879 | 121 |
| 1533 | 251.9 | 130.6 | 884 | 118 |
| 1780 | 237.8 | 144.7 | 894 | 116 |
| 2046 | 224.8 | 157.7 | 897 | 113 |
| 2745 | 195.1 | 187.4 | 915 | 107 |
| Mean... | | | 887 | |

Temperature 40°. Globe II.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^{10}.$ | $K_1 \times 10^7.$ |
|-----------|-------------|-----------|-----------------------|--------------------|
| 0 | 376.3 | | | |
| 675 | 368.4 | 7.9 | 844 | 136 |
| 1420 | 361.9 | 14.4 | 745 | 119 |
| 2055 | 356.2 | 20.1 | 730 | 116 |
| 2730 | 350.5 | 25.8 | 716 | 113 |
| 4170 | 338.6 | 37.7 | 710 | 110 |
| 5600 | 327.2 | 49.1 | 712 | 108 |
| 7040 | 317.4 | 58.9 | 700 | 105 |
| Mean... | | | 722 | |

No correction has been applied for change of barometric pressure, or for the change of pressure of the oxygen during the decomposition ; for, as will be seen later, the variations thus caused are within the limits of experimental error.

It will be noted that the results are not in close accordance with either a first or second order reaction; they are, however, considerably nearer the second than the first.* With one exception (at 40°) the value of $\frac{x}{t(a-x)a}$ rises steadily throughout the experiment.

In the experiment at 40° the amount of ozone decomposed is very small and the measurements extend over several days, so that the decrease in the "constant" may be due to experimental error.

The rate of decomposition increases roughly 10 times for a rise of temperature of 20° at the lower temperatures, and somewhat less rapidly at the higher temperatures.

Effect of varying the Extent of the Glass Surface.—Globe I was packed with short pieces of glass tube of a total area of about 1120 sq. cm. The internal area of the globe was about 240 cm., so that the area of the glass with which the ozone was in contact was nearly six times as large as before.

Temperature 119°·9.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^6.$ | <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^6.$ |
|-----------|-------------|-----------|--------------------|-----------|-------------|-----------|--------------------|
| 0 | 272·5 | | | 4 | 176·2 | 96·3 | 501 |
| 1 | 240·3 | 32·2 | 492 | 6 | 149·4 | 123·1 | 504 |
| 2 | 213·5 | 59·0 | 507 | 11 | 109·3 | 163·2 | 498 |
| 3 | 193·7 | 78·8 | 498 | | | Mean.... | 500 |

The corresponding mean value for the globe with the tubes is 117×10^{-6} ; thus the rate of decomposition was 4·27 as fast. Both the bulb and the tubes were made of soft soda glass. It will be noted that the rate appears much more constant owing to the increased glass surface, but this may be due simply to the increased rate and consequent shortening of the time intervals.

A similar experiment at about 80° gave the following result:—

Temperature 79°·9. Globe II.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^6.$ | <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^6.$ |
|-----------|-------------|-----------|--------------------|-----------|-------------|-----------|--------------------|
| 0 | 308·0 | | | 6 | 166·0 | 142·0 | 463 |
| 1 | 268·8 | 39·2 | 473 | 8 | 144·3 | 163·7 | 460 |
| 2 | 238·2 | 69·8 | 476 | 13 | 107·5 | 200·5 | 466 |
| 3 | 215·2 | 92·8 | 467 | 23 | 68·1 | 239·9 | 497 |
| 4 | 196·2 | 111·8 | 462 | | | | |

* Cf. Warburg, 'Sitzungsberichte der Königl. Preuss. Akad. Wiss. Berlin,' 1901, vol. 48, p. 1126.

The mean rate with the same globe at 80° is 8.04×10^{-6} , so that at this temperature the rate was increased nearly 60 times by the glass tubes.

In another experiment the globe was loosely packed with glass wool, with the following result:—

Temperature 40° . Globe III.

| $t.$ | $a-x.$ | $x.$ | $K_2 \times 10^7.$ | $t.$ | $a-x.$ | $x.$ | $K_2 \times 10^7.$ |
|---------|--------|------|--------------------|------|--------|-------|--------------------|
| 0 | 283.4 | | | 55 | 213.1 | 70.3 | 212 |
| 5 | 275.1 | 8.3 | 213 | 70 | 199.4 | 84.0 | 212 |
| 10 | 266.8 | 16.6 | 220 | 90 | 181.1 | 102.3 | 221 |
| 20 | 252.2 | 31.2 | 218 | 120 | 158.8 | 124.6 | 231 |
| 30 | 239.2 | 44.2 | 217 | 150 | 140.7 | 142.7 | 239 |
| 40 | 228.6 | 54.8 | 211 | 210 | 109.8 | 173.6 | 266 |
| Mean... | | | | | | | 224 |

The normal rate for the globe was not determined at this temperature, but at 100° it was 0.00013. Calculating from the ratio of the rates observed with Globe II, this gives a rate 1.74×10^{-7} at 40° , so that the presence of the glass wool increased the rate of decomposition 129 times.

The effect of a porous substance was next tried, the globe being filled with pieces of clay-pipe stem. The rate of decomposition was then so rapid (no doubt owing to the very large surface) that it was found impossible to measure it, even at the ordinary temperature.

In order to obtain a rate that would be measurable, six pieces of pipe stem of about 2 inches in length were placed at the bottom of the globe. The following numbers were then obtained:—

Temperature $99^{\circ}.7$.

| $t.$ | $a-x.$ | $K_1 \times 10^4.$ | $t.$ | $a-x.$ | $K_1 \times 10^4.$ |
|------|--------|--------------------|------|--------|--------------------|
| 0 | 188.2 | | 5 | 85.6 | 684 |
| 1.25 | 155.6 | 661 | 7 | 63.3 | 676 |
| 2 | 138.1 | 672 | 9 | 46.6 | 674 |
| 3 | 117.8 | 678 | 14 | 22.0 | 666 |
| 4 | 100.0 | 687 | 24 | 5.1 | 653 |

Temperature $60^{\circ}.1$.

| $t.$ | $a-x.$ | $K_1 \times 10^4.$ | $t.$ | $a-x.$ | $K_1 \times 10^4.$ |
|------|--------|--------------------|------|--------|--------------------|
| 0 | 302.7 | | 7 | 150.1 | 435 |
| 1 | 273.8 | 435 | 9 | 123.0 | 435 |
| 2 | 247.0 | 442 | 15 | 70.6 | 421 |
| 3 | 222.0 | 449 | 26 | 27.3 | 402 |
| 4 | 200.4 | 448 | 36 | 11.2 | 398 |
| 5 | 181.3 | 445 | | | |

These numbers extend over a wide range and clearly indicate a reaction "of the first order."

The effect of certain metallic oxides was then tried; a few grammes of the oxide were placed at the bottom of the globe. For each change of material, the globe was cut at the neck and resealed after the introduction of the substance.

Temperature 99°·7. About 20 grammes granulated CuO in Globe.

| $t.$ | $a-x.$ | $x.$ | $K_2 \times 10^5.$ | $K_1 \times 10^4.$ |
|------|--------|-------|--------------------|--------------------|
| 0 | 257·3 | | | |
| 1 | 208·3 | 49·0 | 91 | 917 |
| 2 | 173·5 | 83·8 | 94 | 856 |
| 3 | 147·6 | 109·7 | 96 | 804 |
| 4 | 126·6 | 130·7 | 100 | 770 |
| 5 | 109·4 | 147·9 | 105 | 743 |
| 6 | 95·0 | 162·3 | 110 | 721 |
| 7 | 83·2 | 174·1 | 116 | 700 |
| 9 | 63·3 | 194·0 | 132 | 677 |
| 11 | 47·4 | 209·9 | 156 | 668 |
| 16 | 23·2 | 234·1 | 245 | 653 |
| 21 | 10·7 | 246·6 | 427 | 657 |

The numbers show that the reaction is in this case much nearer first order than second, but is not in close agreement with either. In another experiment at a lower temperature, a good first order constant was obtained :—

Temperature 40°·5. About 20 grammes granulated CuO in Globe.

| $t.$ | $a-x.$ | $K_1 \times 10^4.$ | $t.$ | $a-x.$ | $K_1 \times 10^4.$ |
|------|--------|--------------------|------|--------|--------------------|
| 0 | 342·6 | | 7 | 196·0 | 346 |
| 1 | 314·8 | 368 | 8 | 181·3 | 345 |
| 2 | 289·9 | 362 | 10 | 155·2 | 344 |
| 3 | 266·6 | 363 | 12 | 134·7 | 338 |
| 4 | 247·5 | 353 | 17 | 93·3 | 332 |
| 5 | 227·6 | 355 | 28 | 38·6 | 339 |
| 6 | 211·0 | 351 | 38 | 15·2 | 356 |

A similar result was obtained with magnesia, but the rate was so fast that it was very difficult to measure.

Temperature 40°. About 10 grammes MgO.

| $t.$ | $a-x.$ | $K_1 \times 10^3.$ | $t.$ | $a-x.$ | $K_1 \times 10^3.$ |
|------|--------|--------------------|------|--------|--------------------|
| 0 | 34·1 | | 3 | 7·7 | 215 |
| 1 | 20·9 | 213 | 4 | 5·0 | 208 |
| 2 | 12·4 | 220 | 7 | 1·9 | 179 |

Manganese peroxide also decomposes ozone at an extremely rapid rate, as shown by the following results :—

Temperature 40°. 10 grammes MnO_2 , in small lumps, in Globe.

| $t.$ | $a-x.$ | $K_1 \times 10^3.$ | $t.$ | $a-x.$ | $K_1 \times 10^3.$ |
|------|--------|--------------------|------|--------|--------------------|
| 0.0 | 151.8 | | 2.0 | 27.8 | 367 |
| 0.5 | 102.0 | 345 | 2.5 | 17.6 | 372 |
| 1.0 | 67.0 | 354 | 3.5 | 6.6 | 386 |
| 1.5 | 42.7 | 367 | | | |

Temperature 15°.4. 10 grammes MnO_2 .

| $t.$ | $a-x.$ | $K_1 \times 10^3.$ | $t.$ | $a-x.$ | $K_1 \times 10^3.$ |
|------|--------|--------------------|------|--------|--------------------|
| 0.0 | 149.7 | | 3.5 | 32.2 | 190 |
| 0.5 | 119.4 | 195 | 4.5 | 21.0 | 189 |
| 1.0 | 94.8 | 198 | 5.5 | 13.6 | 189 |
| 1.5 | 75.7 | 197 | 7.5 | 6.3 | 183 |
| 2.5 | 49.2 | 193 | 9.5 | 2.1 | 195 |

Lead peroxide, on the other hand, was found to have comparatively little effect on the rate of decomposition. Commercial lead peroxide was found to absorb ozone, no doubt owing to the presence of lower oxides. The following numbers were obtained with specially purified peroxide, which had been allowed to stand in the presence of ozone :—

Temperature 60°. 1 gramme PbO_2 , in Powder.

| $t.$ | $a-x.$ | $x.$ | $K_2 \times 10^8.$ | $K_1 \times 10^5.$ |
|------|--------|-------|--------------------|--------------------|
| 0 | 421.4 | | | |
| 17 | 396.7 | 24.7 | 869 | 154 |
| 37 | 371.2 | 50.2 | 867 | 149 |
| 57 | 347.4 | 74.0 | 887 | 147 |
| 87 | 316.0 | 105.4 | 910 | 144 |
| 167 | 248.6 | 172.8 | 987 | 137 |
| 207 | 221.7 | 199.7 | 1033 | 135 |

The normal rate at 60°, calculated in the same way as for 40°, is 209×10^{-8} .

Effect of Metallic Surfaces.—Consistent results were not obtained unless the metal had been previously heated in the presence of ozone.

The normal rate for the globe is 1220×10^{-7} , so that the presence of the platinum appears actually to diminish the rate. It is probable that the

normal rate for the globe had changed owing to the alteration in the neck during the opening and resealing.

Temperature 99°·7. Total Area of Surface of Platinum Foil, 19·5 sq. cm.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^7.$ | <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^7.$ |
|-----------|-------------|-----------|--------------------|-----------|-------------|-----------|--------------------|
| 0 | 435·0 | | | 9 | 360·0 | 75·0 | 532 |
| 1 | 425·6 | 9·4 | 508 | 14 | 328·8 | 106·2 | 530 |
| 2 | 417·2 | 17·8 | 490 | 19 | 300·5 | 134·5 | 541 |
| 3 | 407·9 | 27·1 | 509 | 24 | 275·7 | 159·3 | 554 |
| 5 | 391·2 | 43·8 | 515 | 34 | 236·6 | 198·4 | 567 |
| 7 | 375·7 | 59·3 | 518 | 56 | 178·8 | 256·2 | 588 |

Similar results were obtained in the case of nickel :—

Temperature 99°·8. Total Area of Surface of Nickel Foil, 71·5 sq. cm.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^7.$ | $K_1 \times 10^4.$ |
|-----------|-------------|-----------|--------------------|--------------------|
| 0 | 365·8 | | | |
| 2 | 350·7 | 15·1 | 588 | 92 |
| 4 | 336·0 | 29·8 | 606 | 93 |
| 10 | 295·0 | 70·8 | 656 | 93 |
| 18 | 254·0 | 111·8 | 668 | 88 |
| 30 | 207·4 | 158·4 | 696 | 82 |
| 52 | 155·6 | 210·2 | 710 | 71 |
| 72 | 124·6 | 241·2 | 735 | 65 |
| 112 | 86·0 | 279·8 | 794 | 56 |

Some experiments were carried out with silver foil, but the rate of decomposition could not be measured owing to the gradual oxidation of the silver to peroxide by the action of the ozone.

An experiment with platinum black showed an acceleration of the rate of decomposition, though not a large one, and a "second order" constant was obtained.

Temperature 99°·7. Globe VI. About 2 grammes Platinum Black.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^6.$ | <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^6.$ |
|-----------|-------------|-----------|--------------------|-----------|-------------|-----------|--------------------|
| 0 | 98·8 | | | 23 | 59·0 | 39·8 | 297 |
| 3 | 89·8 | 9·0 | 338 | 33 | 50·6 | 48·2 | 292 |
| 8 | 79·2 | 19·6 | 313 | 53 | 38·0 | 60·8 | 305 |
| 13 | 70·6 | 28·2 | 311 | 88 | 26·5 | 72·3 | 314 |

The normal rate for this globe was $81·9 \times 10^{-6}$.

Influence of Moisture.—A trace of moisture is known to be held by a glass surface, even at temperatures above 100°. An experiment was therefore

made to discover whether the moisture so held was sufficient to have an appreciable effect on the rate of decomposition. The globe was heated in an air bath at about 400° , and pumped out several times. It was then placed in the calcium chloride bath, and an experiment conducted as usual. The mean rate was 0.000055, while the rate found without the previous heating was 0.000053, a difference which may be ascribed to experimental error.

A series of experiments was made with varying quantities of moisture in the globe. The water vapour was introduced from a nitrometer containing water. This was well shaken to ensure the saturation of the air with water vapour; it was then connected with the exhausted globe, and the required quantity of moist air quickly admitted, the pressure of the air being maintained constant.

In one experiment air was passed from the nitrometer through a series of four bulbs containing water, placed in a water bath, and thence into the decomposition globe. In this way, 2.77 milligrammes of water vapour were introduced.

The general effect of the moisture is to quicken the rate of decomposition, and the numbers are in much better accord with a second order constant than those obtained with dry ozone. The following is a good example:—

Temperature $119^{\circ}5$. Globe I. 0.69 milligramme Water in Globe.

| t . | $a-x$. | x . | $K_2 \times 10^6$. | t . | $a-x$. | x . | $K_2 \times 10^6$. |
|-------|---------|-------|---------------------|-------|---------|-----------|---------------------|
| 0 | 329.0 | | | 8 | 225.3 | 103.7 | 175 |
| 1 | 311.3 | 17.7 | 173 | 13 | 188.7 | 140.3 | 174 |
| 2 | 294.0 | 35.0 | 181 | 23 | 142.9 | 186.1 | 172 |
| 3 | 279.9 | 49.1 | 178 | 33 | 114.0 | 215.0 | 174 |
| 4 | 266.1 | 62.9 | 180 | 53 | 80.8 | 248.2 | 176 |
| 6 | 244.2 | 84.8 | 176 | | | Mean..... | 176 |

The increase in the rate of decomposition is (within the limits of experimental error) proportional to the mass of water vapour present. The mean values of the constants are here given, together with the corresponding quantities of water admitted in milligrammes (m), and the constants calculated from the formula:

$$k = 122 + 135.1m.$$

The normal rate for the globe was 0.000122.

| m . | $K_2 \times 10^6$. | k . | m . | $K_2 \times 10^6$. | k . |
|-------|---------------------|-------|-------|---------------------|-------|
| 0.0 | 122 | | 0.58 | 209 | 200 |
| 0.75 | 214 | 223 | 1.40 | 310 | 324 |
| 0.69 | 176 | 215 | 2.77 | 515 | 496 |

Effect of Nitric Oxide.—An attempt was made to measure the rate of decomposition of ozone after the addition of a small quantity of nitric oxide. Several trials were necessary in order to find a suitable temperature, and how much nitric oxide could be added without decomposing the ozone too quickly. Finally, measurements were made at $119^{\circ}\cdot 1$ after the addition of 0.2 c.c. nitric oxide (at 15° and 800 mm.). The nitric oxide was made in a nitrometer from potassium nitrate and sulphuric acid over mercury, and was forced into the globe, which already contained ozonised oxygen at a constant temperature.

The following is the result:—

| $t.$ | $a-x.$ | $x.$ | $K_2 \times 10^5.$ | $K_1 \times 10^3.$ |
|------|--------|------|--------------------|--------------------|
| 0 | 58.5 | | | |
| 1 | 43.4 | 15.1 | 595 | 130 |
| 2 | 30.5 | 28.0 | 785 | 141 |
| 3 | 21.5 | 37.0 | 981 | 145 |
| 4 | 13.7 | 44.8 | 1397 | 158 |

The rate of decomposition was thus extremely fast, and, so far as it could be followed, appeared to be roughly of the first order.

In a similar experiment with 1 c.c. of nitric oxide, the decomposition was too rapid for measurements to be made.

Attempts were made to follow the change completely at a lower temperature; 0.8 c.c. nitric oxide, contained in a tube between two stop-cocks, was allowed to diffuse into a bulb containing 150 c.c. ozonised oxygen, the whole being placed in a water bath at 10° .

The change of pressure was measured by a sulphuric acid gauge connected with the upper part of the bulb. It was found that a decrease of pressure of 47 mm. of sulphuric acid took place, the pressure then remaining constant. This represents a decrease of about 1 per cent. in the volume, and is more than would be accounted for by the combination of nitric oxide either with oxygen or ozone to form nitrogen peroxide. Probably this is due to condensation of nitrogen tetroxide in the liquid state.

At 50° no rapid decomposition of the ozone was observed after introducing 1 c.c. of nitric oxide, while at 100° the rate was accelerated but very irregularly.

Effect of Varying the Pressure of the Oxygen.—A series of experiments was made at various pressures with the complete apparatus as shown in fig. 1. The large globe F was connected with B, and brought down to the required pressure by means of a Fleuss pump. A was exhausted and the ozone admitted in the usual way, until the pressure in A was known to be

in excess of that required. The globe A was connected with F until the pressure was equalised; it was then connected with the gauge, the stop-cock H was closed, and readings were taken as usual. The total amount of ozone was also determined as before.

Some manganese peroxide was placed at the bottom of the globe F in order to decompose the ozone admitted.

The general character of the results is the same as those at atmospheric pressure, *i.e.*, they are approximately of the second order, but the rate increases towards the end of the experiment. The mean results are given in the following table, together with two at ordinary pressure for comparison:—

Temperature 99°·7.

| Pressure. | $K_2 \times 10^7$. | Pressure. | $K_2 \times 10^7$. | Pressure. | $K_2 \times 10^7$. |
|-----------|---------------------|-----------|---------------------|-----------|---------------------|
| 755 | 531 | 583 | 788 | 449 | 776 |
| 758 | 550 | 550 | 720 | 375 | 888 |
| 638 | 631 | 482 | 737 | 304 | 916 |
| 593 | 763 | 468 | 851 | 276 | 1070 |

Effect of Diluting with Air.—A few experiments were made in which the pressure of the oxygen was diminished by the addition of air. The large globe F was exhausted to approximately $\frac{1}{2}$ an atmosphere; the globe A was then filled as usual and allowed to blow off into F. The following are the results:—

Temperature 99°·8.

| Pressure of oxygen. | $K_2 \times 10^6$. |
|---------------------|---------------------|
| mm. | |
| 467 | 155 |
| 458 | 165 |
| 462 | 152 |

Normal rate for the globe (VI), 81.9×10^{-6} .

Discussion of Results.

Effect of Temperature.—The relation between rate of decomposition and temperature may be expressed by the formula $\log k = a + bt$, a formula found by one of us to express the connection between the rate of evaporation of ammonia from aqueous solution and temperature* and used also by Van't Hoff.†

* 'Chem. Soc. Trans.,' 1898, p. 524.

† 'Vorlesungen über theoretische und physikalische Chemie,' 1901, vol. 1, p. 224.

Putting $a = 2.86$ and $b = 0.05$, the following numbers are obtained :—

| Temperature. | $\log k$ (found). | $\log k$ (calculated). |
|--------------|-------------------|------------------------|
| 40 | 2.86 | 2.86 |
| 60 | 3.95 | 3.86 |
| 80 | 4.91 | 4.86 |
| 100 | 5.74 | 5.86 |
| 120 | 6.86 | 6.86 |

It occurred to us that the decomposition might take place instantaneously at the surface of the glass (or other substance), and that the rate measured was simply the rate of diffusion of the gas towards the surface. These results, however, show that the idea is untenable, for the rate would in that case vary as the square root of the absolute temperature.

Effect of Varying Extent of Surface.—It has been shown that the rate depends on the extent of the surface, but it could not be shown that it is proportional to the surface. It must be remembered, however, that it is impossible to vary the extent of the surface and yet ensure its uniformity. With a very large surface a much better second order constant is obtained; this may be due to the almost entire prevention of any effect of diffusion, but we are inclined to think that it is caused simply by the increased rapidity and shorter range of the reaction.

Effect of Oxides.—From the results given it is impossible to conclude that the peroxides used act as carriers of oxygen, for lead peroxide has but little effect, whereas manganese peroxide accelerates the reaction enormously. Moreover, copper oxide and magnesium oxide have a great effect in increasing the rate of decomposition. Neither can the effect be due entirely to the extent of the surface of the oxide. Manganese peroxide in lumps had more effect than magnesia in powder, but lead peroxide in powder had very little influence. With these oxides a good first order constant was obtained, *i.e.*, the rate of decomposition was proportional to the pressure of the ozone, and it seems to us that the only conclusion to be drawn is that the real factor is the rate of absorption or condensation of ozone on the surface of the oxide.

Effect of Metallic Surfaces.—Of the metals tried, the effect in each case was small, and appeared to be a diminution of the rate of decomposition. This is entirely different from the effect of metals on the combination of hydrogen and oxygen as found by Bone and Wheeler;* the latter was attributed, however, to the occlusion of hydrogen.

Effect of Certain Vapours.—It has been shown that water vapour

* *Loc. cit.*

accelerates the rate of decomposition, and that the effect is roughly proportional to the quantity of water present. Ozone is not known to have any action on water vapour, and it appears probable that this effect is due to the deposition of moisture on the surface of the glass, owing to which the ozone would be more rapidly condensed. These results appear to be directly in opposition to those of Shenstone, who found that ozone was more stable in the presence of moisture (this was, however, at a much lower temperature).

The action of nitric oxide is much greater than that of water if a sufficiently high temperature is employed (100° — 120°), and it would seem a reasonable explanation that the nitric oxide acts as a carrier of oxygen, being continually oxidised to the peroxide, and reduced again by the action of the ozone until the latter is entirely decomposed.

Effect of Variation of the Oxygen Pressure.—The rate of decomposition has been shown to be a linear function of the pressure of the oxygen; this cannot be caused by the reversibility of the reaction, for it has been shown to be irreversible for all practical purposes. S. Jahn* made somewhat similar experiments, varying the pressure of the oxygen by dilution with air, and found that the rate varies approximately inversely as the oxygen pressure, a result confirmed by experiments of our own. From these results Jahn deduces that a secondary reaction takes place, $O_3 + O = 2O_2$. We find that on varying the pressure without the intervention of another gas, the rate is not affected to the same extent, *e.g.*, a variation of the pressure from 600 mm. to 300 mm. caused the rate to vary from 0.0000685 to 0.000097. We are inclined to think that Jahn's conclusion is not justifiable, and that the variation of the oxygen pressure produces a difference in the gas-film on the surface and so alters the rate. It can only be said at present that the mechanism of the process is not understood.

Reversibility of the Reaction.—Attempts were made to synthesise ozone by passing a slow stream of oxygen through a combustion tube heated in a gas furnace. The tube was bent at the outlet and dipped in a solution of potassium iodide and starch. No ozone could be detected. The experiment was then repeated with the following substances in the tube respectively:—pipe stems, iron nails, platinised asbestos, manganese peroxide: traces of ozone were formed with the last named, but none could be detected with the others. The solution became brown, and on letting it stand a blue colour was developed. No ozone was found unless the temperature was high (a low red heat), and the oxygen was passed through quickly. With a slow stream probably the ozone formed was decomposed before leaving the tube.

* 'Zeit. anorg. Chem.,' 1906, vol. 48, p. 260.

In the following experiments oxygen was heated in a globe for many hours in order to discover whether any ozone could be formed in this way :—

| Temperature. | Time of heating, etc. | Result. |
|--------------|------------------------------|-----------------------------|
| ° | | |
| 130 | 24 hours | Nil |
| 100 | 17 " | " |
| 100 | 4 days with Pt black | " |
| 100 | 4 days with MnO ₂ | " |
| 100 | 7 days | Trace of O ₃ (?) |
| 100 | 14 " | " " |

It is somewhat doubtful whether any ozone was detected, for a blank experiment with oxygen (not heated) gave nearly as much colour, *i.e.*, a brownish tint, developing into blue on standing some hours.

Experiments were also made to ascertain whether ozone could be completely decomposed by heat ; the following are the results :—

| Temperature. | Time of heating. | Result. |
|--------------|------------------|---|
| ° | | |
| 100 | 18 hours | 1·7 milligrammes O ₃ remained. |
| 100 | 5 days | 0·07 " " |
| 100 | 14 " | Trace " " |

In the last experiment there was no doubt that a trace of ozone remained after a fortnight's heating ; it seems probable that it had come into equilibrium. We conclude from these experiments that the decomposition of ozone by heat is not completely irreversible at 100°, but that the reverse reaction is so small that it is difficult to detect.

Summary.—The rate of decomposition of ozone has been measured under various conditions with the following results :—

1. In a glass vessel the reaction is approximately of the second order.
2. The relation between the rate of decomposition and temperature may be expressed by the formula $\log k = a + bt$.
3. The rate of decomposition is very largely influenced by the extent of the surface with which the ozone is in contact.
4. The reaction is of the first order when the ozone is in contact with a porous substance (clay-pipe stems) or some oxides.
5. Metallic surfaces have but little effect on the decomposition.
6. Water vapour accelerates the decomposition, and the acceleration is proportional to the amount present.

7. Nitric oxide greatly accelerates the decomposition.
8. The rate of decomposition is a linear function of the oxygen pressure. A greater effect is produced by diluting with nitrogen than by simply reducing the pressure of the oxygen.
9. At 100° the reaction appears to be very slightly reversible.
10. Finally, the decomposition appears to take place mainly (if not entirely) at the surfaces with which the ozone is in contact, and pressure measurements give no indication of the number of molecules reacting.

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*Effects of Self-induction in an Iron Cylinder when traversed
by Alternating Currents.**

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In a previous paper† the effects of self-induction in an iron cylinder were studied when a continuous current flowing through the cylinder in a direction parallel with its axis of figure was suddenly reversed and again maintained steady. In the experiments reported in the present paper the currents in the cylinder were made to alternate in the following manner. A continuous current dynamo, capable of giving currents up to 2000 amperes or more, was weakly excited and its brushes were short-circuited by the cylinder to be experimented upon in series with the shunt of a moving-coil ampere-meter. The brushes were moved round the commutator by aid of a worm and worm-wheel from the position of maximum to that of zero current. The field was then reversed and the brushes moved back to their initial position.

By continuing these operations an alternating current was caused to flow through the cylinder, and its periodic time was controlled by the speed at which the brushes were moved. The worm axle was uniformly rotated by hand at a speed determined by the operator listening to a seconds clock.

* In connection with this research, I wish to acknowledge a grant voted to me by the Council of the Royal Society out of the Government Grant Fund.

† 'Roy. Soc. Proc.,' A, vol. 78, p. 22, 1906.